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LEAN-BURN NATURAL GAS ENGINE EXHAUST REMEDIATION USING NANOSTRUCTURED CATALYSTS AND COATINGS

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Abstract

We have developed nanocrystalline catalytic systems with excellent thermal stability that reduce NO, CH_4 and CO emissions from exhaust streams containing excess oxygen. Magnesium oxide, yttrium oxide and samarium oxide catalysts were synthesized using a controlled wet-chemical precipitation technique. This process produces nanocrystalline, high surface area metal oxide powders that can be easily coated onto monoliths and substrates. Greater than 50% conversion of NO to N_2 was achieved in excess O_2 at high space velocities with the nanocrystalline oxide catalysts. Nanostructured barium hexaaluminate coated with manganese oxide was used to aid in the complete oxidation of CO and CH_4. The nanocrystalline oxide systems have superior hydrothermal stability compared to noble metal and zeolitic catalysts. Presence of water vapor in the feed stream resulted in only a slight loss of activity for the nanocrystalline Y_2O_3 system, the full activity of which was restored upon removal of water from the feed stream.

Introduction

The development of catalytic materials that can simultaneously reduce NO_X, and oxidize CO and hydrocarbons has been pursued for decades. So-called three-way catalysts are successfully used in automotive exhaust treatment, but are only effective at reducing NO_X to N_2 at stoichiometric (λ=1) or fuel-rich (λ<1) conditions. New challenges for automotive catalytic systems have arisen in the past few years in response to new technologies that aim to increase automobile fuel efficiency and decrease exhaust emissions.

The use of natural gas (>90% methane) as a fuel source has actively been investigated because of the lower global warming impact of methane combustion compared to gasoline combustion. The combustion of natural gas produces 54 g of CO_2 per MJ, whereas the combustion of gasoline releases 74 g CO_2/MJ [1]. The use of natural gas also allows engine operation at a higher compression ratio (due to the higher

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octane number of methane) and this increases the thermal efficiency of the engine [2]. Unfortunately, current noble metal-based catalytic converters are not as efficient at oxidizing unburnt methane in the exhaust stream as they are at converting longer chain hydrocarbons that are typically found in the exhaust of conventional gasoline engines. Natural gas vehicles equipped with such conventional catalysts are thus only able to meet non-methane hydrocarbon (NMHC) emission standards, but not the total hydrocarbon (THC) emission standards [3].

The application of lean-burn technology has been touted as the most efficient approach to minimizing exhaust emissions from small and medium engines [1]. This technology involves engine operation under fuel-lean conditions. The presence of excess air results in more complete combustion at a lower combustion temperature, which also reduces NO_X formation during combustion. Although this technique significantly lowers engine-out NO_X emissions, further removal of NO_X from the exhaust gas is required in order to reach regulated ultra-low emissions levels. However, conventional three-way catalysts are unable to effectively reduce exhaust levels of NO_X in the presence of even small amounts of excess oxygen ($\lambda > 1.01$) [4,5].

Thus, there is a need for developing catalytic systems that are able to oxidize CH_4 and CO and reduce NO_X to N_2 under oxidizing conditions. While several zeolitic materials have been found to catalyze these reactions, high-temperature hydrothermal stability is a problem for these catalysts [6-8]. Thermal stability for automotive catalysts is required well beyond their usual operating temperatures of 400 to 500°C, due to temperature excursions that may occur during heavy acceleration or engine misfiring. One of the major issues with three-way catalyst durability is the thermal deactivation that takes place at temperatures of 900°C and higher [4,9].

Group IIIB metal oxides [10] and lanthanide oxides [11] have been reported to be very active for the catalytic reduction of nitrogen oxides under oxidizing conditions. They also have excellent activity for the oxidation of carbon monoxide and hydrocarbons, and possess good hydrothermal stability when prepared in a nanocrystalline form [10]. We have focussed our work on nanocrystalline magnesium oxide, yttrium oxide and samarium oxide as catalysts for the reduction of NO_X to N_2 in excess O_2. A second component has been examined as a catalyst to promote the complete oxidation of CO and CH_4. Noble metal oxidation catalysts lack the high-temperature stability required for this application, so we have chosen to employ nanostructured barium hexaaluminate (BHA) coated with transition metal oxide as the oxidation catalyst.

Experimental

Magnesium oxide, yttrium oxide and samarium oxide catalysts were synthesized using a wet-chemical precipitation technique. This consisted of mixing aqueous solutions (0.25 M) of metal nitrate ($Mg(NO_3)_2$ – 99%, Aldrich; $Y(NO_3)_3$ – 99.99%, Alfa Aesar; $Sm(NO_3)_3$ – 99.9%, Alfa Aesar) and tetraethylammonium hydroxide (35 wt%, Aldrich) at a pH between 12 and 13. The precipitate was then aged for 24 hours. After thoroughly washing the precipitate with ethanol, the material was air-dried, ground in a mortar and pestle, and then oven-dried at 120°C to remove any residual alcohol. The powder was calcined in flowing oxygen for 4 hours at 900°C to

convert the hydroxide or hydroxynitrate precipitate to a pure oxide phase that is stable at the high reaction temperatures.

The barium hexaaluminate support was prepared using a reverse emulsion-assisted sol-gel technique [12,13]. Barium isopropoxide was prepared by reacting metallic barium (99.8%, Aldrich) with isopropanol (99.99%, Mallinckrodt) by refluxing under air-free conditions at 70°C for 24 hours. Aluminum isopropoxide (99%, Aldrich) was dissolved in hot isopropanol by refluxing at 70°C for 24 hours. Stoichiometric amounts of the solutions containing barium and aluminum isopropoxides were mixed, prior to hydrolysis, in degassed 2,2,4-trimethylpentane (99.9%, Aldrich). A reverse microemulsion with a water:oil weight ratio of 15:85 was prepared by mixing doubly-deionized H_2O, 2,2,4-trimethylpentane and a surfactant mixture. The surfactant mixture contained 67 wt% polyethoxylated linear alcohols (Neodol 91-6, Shell) and 33 wt% 1-pentanol (99.9%, Aldrich). The amount of surfactant added was calculated taking into account the amount of isopropanol and water liberated by the hydrolysis and polycondensation reactions of the alkoxide precursors. The final composition of the emulsion was 12.8 wt% H_2O, 72.5 wt% 2,2,4-trimethylpentane, and 14.7 wt% surfactants.

The solution containing the alkoxide precursors was added drop-wise to the reverse emulsion with slow stirring. The hydrolyzed mixture was allowed to age for 24 hours before recovery by freeze drying. The BHA nanoparticles recovered were washed with isopropanol, supercritically dried, and then calcined at 800°C for 4 hours.

The active MnO_2 coatings were applied onto the surface of the BHA nanoparticles by impregnation. The BHA powders were suspended in H_2O, and then manganese nitrate (99%, Aldrich) was added to the suspension and stirred for 30 minutes. Air was then bubbled through the suspension to promote oxidation of the manganese nitrate on the surface of the BHA nanoparticles. The MnO_2/BHA sample was then air-dried and calcined to 900°C.

Dip-coating was employed to coat the nanocrystalline yttrium oxide catalyst onto a commercially available magnesia-stabilized zirconia monolith. By dip-coating from an aqueous suspension containing 25 wt% nanocrystalline yttrium oxide and 1 wt% polyethylene oxide, a loading of 11 wt% yttrium oxide on the magnesia-stabilized zirconia monolith was achieved. The composite was calcined to 800°C.

Catalyst surface area was determined by N_2 adsorption using a 5-point BET (Brunauer-Emmett-Teller) method on a Micromeritics ASAP 2000 instrument. Phase identification was performed by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer (45 kV, 40 mA, Cu-Kα). Scherrer's analysis of the X-ray peak broadening was employed to determine crystallite size. Transmission electron microscopy (TEM) was performed on a JEOL 2010 microscope. Scanning electron microscopy (SEM) was performed on a JEOL 6320 microscope.

Catalytic activity measurements were obtained at atmospheric pressure under steady-state reaction conditions in a 1/4"-O.D. quartz tube reactor with the catalyst supported on a porous quartz frit. Type K thermocouples were located above and below the catalyst bed, and were used in conjunction with an Omega temperature controller and a Lindberg tube furnace to maintain the catalyst within 2°C of the desired operating temperature. High-purity gases (He, 10.0% O_2-He, 1.48% NO-He, 2.01% CH_4-He and 2.06% CO-He) were metered into the top of the quartz reactor with five

independent MKS mass flow controllers. The reactor effluent was analyzed with a Perkin Elmer Autosystem gas chromatograph equipped with a 10' x 1/8"-O.D. molecular sieve 5A column and a 12' x 1/8"-O.D. Porapak Q chromatographic column. This allowed oxygen, nitrogen, nitrous oxide, methane, carbon dioxide, carbon monoxide and hydrogen in the reactor effluent to be separated and quantified. Carbon balances to within 2.5% were achieved in all runs.

Results and Discussion

The BET surface areas and XRD crystallite sizes of the catalysts, following calcination to 900°C and catalytic testing, are presented in Table 1. The BHA material had a surface area of 248 m²/g and a TEM particle size of approximately 5 nm prior to MnO_2 loading. The crystallite size of the manganese oxide in the 14.7 wt% MnO_2/BHA composite was too small to be determined through XRD. The Y_2O_3-coated magnesia-stabilized zirconia monolith had a specific surface area of approximately 3 m²/g, and a yttrium oxide crystallite size of 29 nm. The low surface area is not unexpected, given the 11 wt% loading of nanocrystalline Y_2O_3, the original 38 m²/g surface area of the unsupported Y_2O_3, and the negligible surface area of the uncoated ceramic monolith.

TABLE 1. Surface area and crystallite size of catalysts

Catalyst	Surface Area, m²/g	Crystallite Size, nm
MgO	71	20
Y_2O_3	38	22
Sm_2O_3	16	31
MnO_2/BHA	167	N/A

Transmission electron micrographs of the Y_2O_3 and MnO_2/BHA catalysts are presented in Figures 1 and 2, respectively. The Y_2O_3 catalyst is composed of submicron-sized aggregates containing primary particles with dimensions on the order of 25 nm. This is in good agreement with the XRD crystallite size of 22 nm. The MnO_2/BHA nanocomposite has a similar aggregate size, but the primary BHA particles are on the order of 5 nm. High-resolution TEM reveals the presence of a crystalline manganese oxide phase on the surface of the amorphous BHA particles (Figure 2b).

Figure 3 shows the microstructure of the Y_2O_3-coated magnesia-stabilized zirconia monolith. The morphology of a heavily coated area of the monolith is shown in Figure 3a. Submicron-sized particles of Y_2O_3 completely cover the magnesia-stabilized zirconia surface. Figure 3b shows a region of slightly lower Y_2O_3 loading, where the highly dense ceramic monolith support of micron-sized grains can be observed through a patchy coating of Y_2O_3 particles.
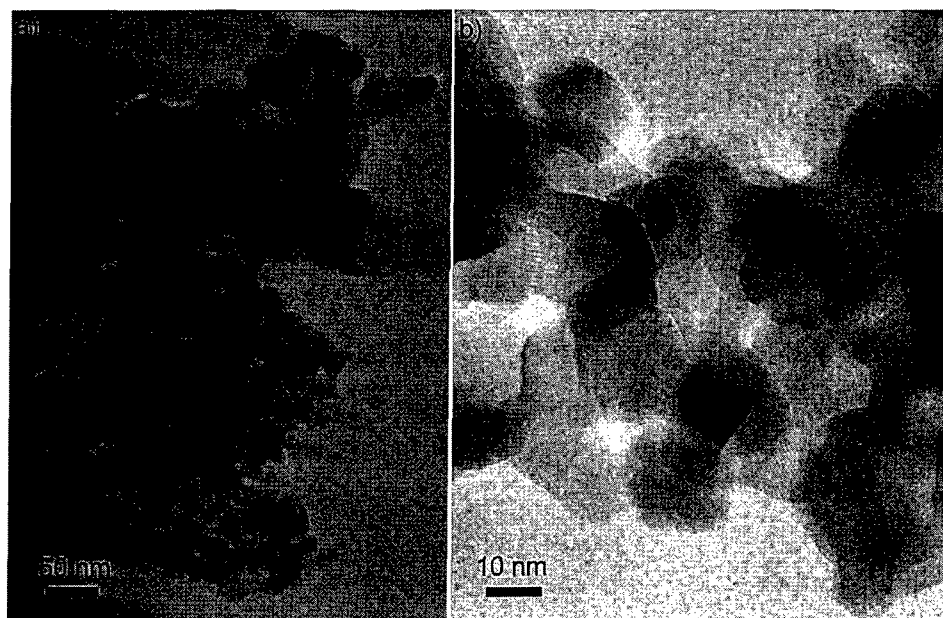
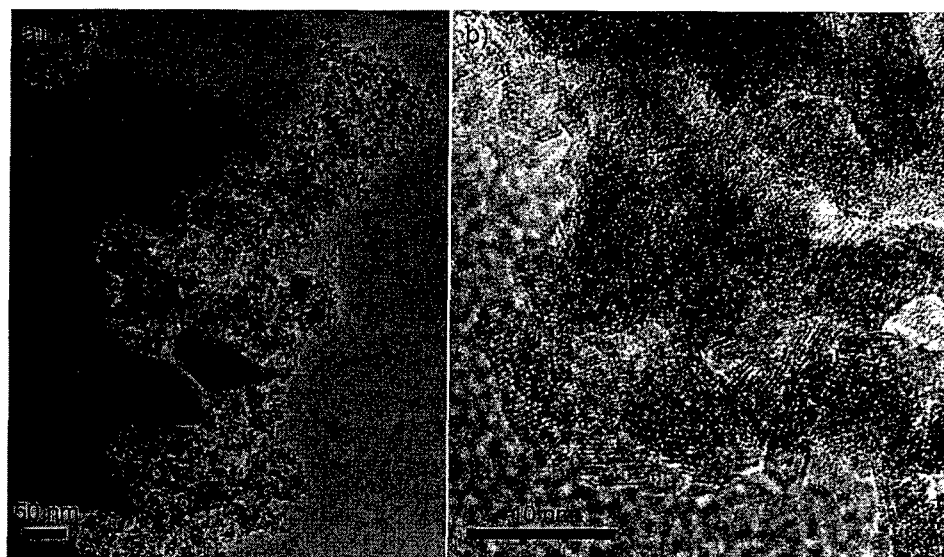*Figure 1.* TEM images of nanocrystalline Y_2O_3.

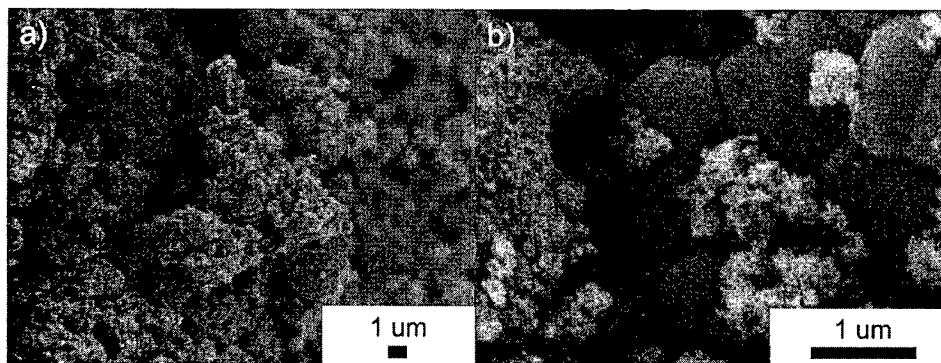*Figure 2.* TEM images of MnO_2/BHA nanocomposite.

Figure 3. SEM images of Y_2O_3-coated magnesia-stabilized zirconia monolith.

The activities of the magnesium oxide, yttrium oxide and samarium oxide catalysts in a gas stream containing 5000 ppm NO, 5000 ppm CO, 5000 ppm CH_4 and 1.67% O_2 at a space velocity of 30 000 h^{-1} are shown in Figures 4 and 5. High removal rates of all undesirable gases can be achieved at temperatures as low as 450°C and are maintained to temperatures above 800°C. For NO removal, samarium oxide is the most active catalyst below 550°C, yttrium oxide is the most active system between 550 and 750°C, and magnesium oxide exhibits the highest activity above 750°C. Hydrocarbon and CO oxidation is best achieved by samarium and yttrium oxides, with magnesium oxide exhibiting significantly lower activity. Yttrium oxide appears to be the most effective overall catalyst, with a large temperature window for NO reduction and relatively low light-off temperatures for oxidation of CO and CH_4.

The temperature range for which these catalysts are most active exceeds the temperatures typically encountered in conventional catalytic converter systems (400-500°C). The high thermal stability of these materials would, however, allow them to be employed in a close-coupled engine exhaust configuration, where the exhaust catalyst is placed near the engine. The higher exhaust temperature in this configuration would allow the operation of the catalyst within its optimal temperature range. An additional benefit of the close-coupled system is decreased cold-start emissions in comparison to the conventional downstream catalytic converter.

The stoichiometric air-to-fuel ratio for methane combustion is 17.1 [3]. Lean-burn natural gas engines typically operate at air-to-fuel ratios of 20 to 27 (λ=1.2-1.6), with corresponding exhaust redox ratios (molar ratio of oxidizing species to reducing species = $C_{O2}/(2C_{CH4} + 0.5C_{CO})$) of 5 to 50 [3]. We have examined the catalytic activity of nanocrystalline yttrium oxide at higher partial pressures of oxygen, and lower partial pressures of NO, CO and CH_4 to determine how the catalyst behaves at redox ratios more representative of actual lean-burn engine exhaust. Figure 6 shows the activity of nanocrystalline Y_2O_3 for NO_X reduction, CH_4 oxidation and CO oxidation in a gas mixture containing 1000 ppm NO, 1000 ppm CH_4, 1000 ppm CO and 0.5-7.5% O_2 (redox ratios of 2-30) at 600°C and a space velocity of 30 000 h^{-1}.
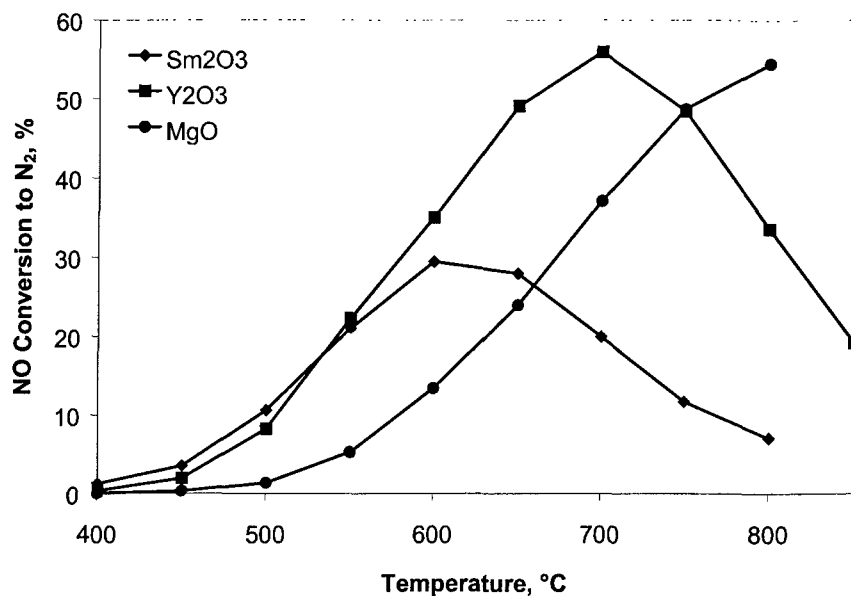
Figure 4. NO reduction activity of nanocrystalline oxide catalysts.
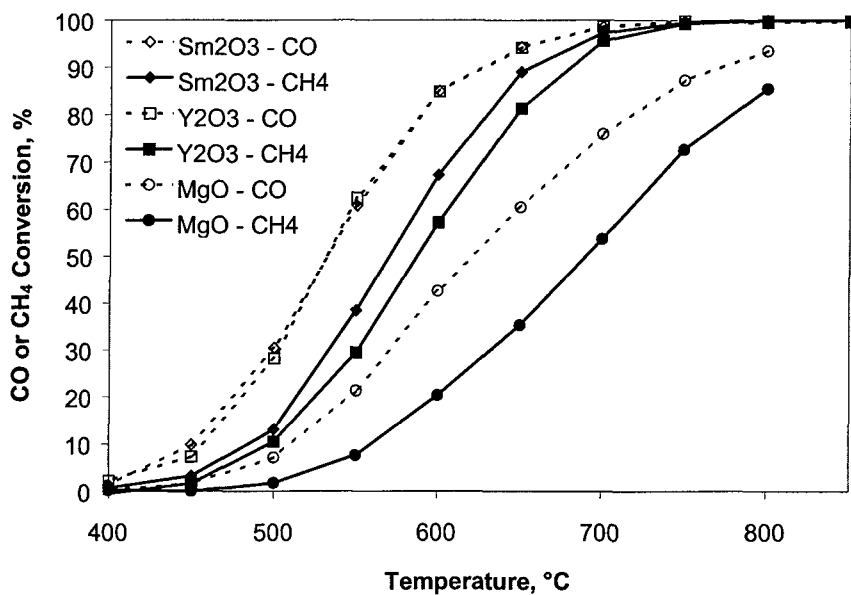

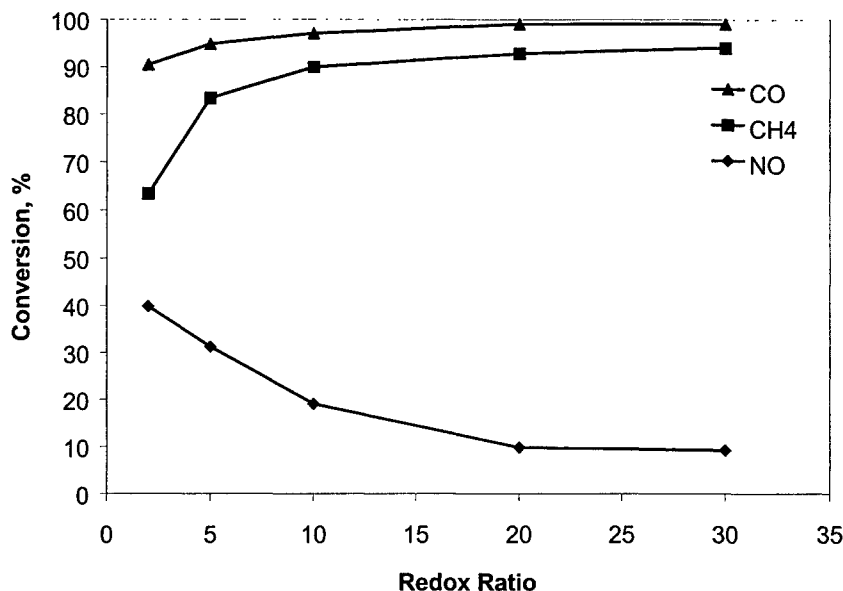*Figure 5.* Activity of nanocrystalline oxide catalysts for oxidation of CO or CH₄.

Figure 6. Effect of redox ratio on the catalytic activity of nanocrystalline Y_2O_3.

Clearly, oxygen has an inhibitory effect on the NO reduction activity, while it enhances the oxidation activity of the yttrium oxide catalyst. The lowered NO reduction activity is due to the increased competition between NO and O_2 for reaction with the reducing agent, CH_4. As the partial pressure of oxygen in the exhaust increases, a larger proportion of the CH_4 reacts nonselectively with O_2 to produce CO_2 and H_2O, and a smaller fraction of the CH_4 reacts with NO through a pathway that ultimately produces N_2. However, even at a redox ratio of 30, substantial NO_X reduction is achieved with the nanocrystalline Y_2O_3 catalyst.

At temperatures below 700°C or redox ratios below 10, significant amounts of CH_4 and CO remain unconverted after passing through the Y_2O_3 catalyst bed. Barium hexaaluminate coated with manganese oxide was added to the catalyst system in order to fully oxidize these unwanted exhaust components. The key to improving oxidation capacity without significantly affecting the reduction activity was to place the additional oxidation catalyst downstream of the nanocrystalline Y_2O_3 catalyst. Through this configuration, the concentration of reducing agents was maximized throughout the Y_2O_3 catalyst bed to promote the reduction of NO_X to N_2. Any unreacted CH_4 or CO exiting the Y_2O_3 catalyst bed was then oxidized downstream over the MnO_2/BHA catalyst bed.

By employing a catalyst system containing 75% Y_2O_3 and 25% MnO_2/BHA by volume, CO conversion was increased from 95% to 100%, while CH_4 conversion

was increased from 83% to 92% at 600°C and a redox ratio of 5. The NO_X reduction activity of the system under these conditions was only lowered slightly from 31% to 26%. The same system was used to remediate a gas stream containing 5000 ppm NO, 5000 ppm CO, 5000 ppm CH_4 and 1.67% O_2 (redox ratio = 1.34) at a space velocity of 30 000 h^{-1} (Figure 7). At these conditions, the NO_X reduction activity was essentially unchanged, while the CH_4 and CO conversions were significantly enhanced. The MnO_2/BHA component of the catalyst system was particularly helpful towards improving CO oxidation at low temperatures.
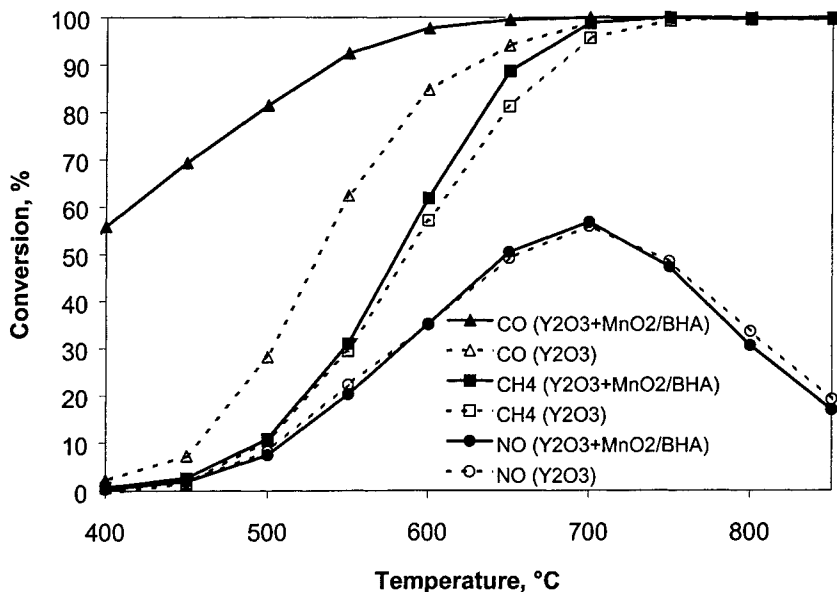

Figure 7. Catalytic activity of (i) the nanocrystalline Y_2O_3 system and (ii) the nanocrystalline Y_2O_3 + MnO_2/BHA system for CO oxidation, CH_4 oxidation and NO reduction.

The successful implementation of a new catalyst for automotive applications requires that the catalytic converter remains active for an exceptionally long time period. The presence of water vapor in the exhaust gas is a major source of problems for many materials that are possible alternatives to the existing three-way catalyst. Steam may induce lattice dealumination and irreversible deactivation in many zeolitic systems at temperatures ranging from 500 to 800°C [8,14]. The catalytic activity of nanocrystalline yttrium oxide was examined in the presence of 1000 ppm NO, 1000 ppm CH_4, 1000 ppm CO, 1.25% O_2 and 3.5% water vapor to characterize the hydrothermal stability of this catalyst. At 650°C, a decrease in NO conversion to N_2 from 25 to 20% was observed upon addition of water vapor to the reactant stream for 12 hours. However, upon removal of the water vapor from the feed stream, the initial

NO reduction activity (25% conversion) was fully restored. Furthermore, no loss of surface area from steaming of the catalyst was observed under these conditions.

The practical application of this multifunctional catalyst system requires that the active catalyst be dispersed on a mechanically and thermally stable support. A ceramic monolith was selected for this purpose because of the high-temperature stability needed for this system. Specifically, a magnesia-stabilized zirconia monolith was employed because it has similar thermal expansion coefficient and crystal structure as yttrium oxide, and will not react with yttrium oxide to form inactive phases. The catalytic activity of the Y_2O_3-coated reticulated monolith in the presence of 5000 ppm NO, 5000 ppm CH_4, 5000 ppm CO and 1.67% O_2 at a space velocity of 6000 h^{-1} is presented in Figure 8. The activity of 11 wt% Y_2O_3-coated monolith is lower than that of the unsupported Y_2O_3 powder catalyst, with complete oxidation of CO and CH_4 requiring temperatures of ~800°C in the former. Improvements in catalytic activity can be realized by an increased loading of the active Y_2O_3 nanocrystals onto the ceramic monolith.
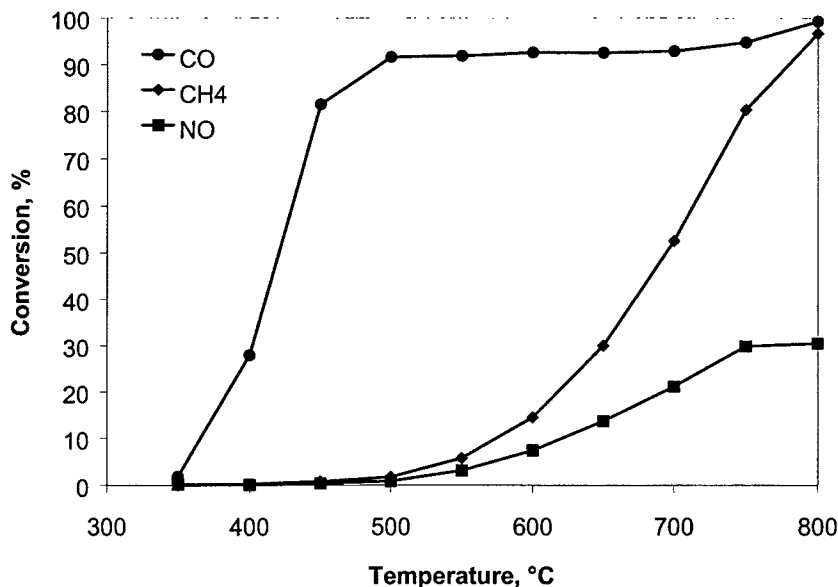

Figure 8. Catalytic activity of 11 wt% Y_2O_3-coated magnesia-stabilized zirconia monolith.

Conclusions

We have found that nanocrystalline yttrium oxide, samarium oxide and magnesium oxide are promising catalysts for the remediation of exhaust streams from lean-burn natural gas engines. 95% conversion of CO, 83% conversion of CH_4 and 31% conversion of NO to N_2 can be achieved by nanocrystalline Y_2O_3 at a redox ratio of 5 at 600°C. Introduction of an additional oxidation catalyst (MnO_2/BHA) downstream of the nanocrystalline Y_2O_3 catalyst significantly improves the oxidation capability of the catalytic system with only a slight decrease in NO_X reduction capability. These nanocrystalline oxide catalysts are thermally stable to at least 900°C, allowing for application in close-coupled exhaust systems. They can be easily applied onto dense ceramic monoliths as nanostructured coatings for practical applications.

Acknowledgments

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